Macromolecules 1993, 26, 1841-1847

Penetrant Transport in Cross-Linked Polystyrene

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Received January 21, 1992; Revised Manuscript Received January 5, 1993

ABSTRACT: Swelling studies of cross-linked polystyrene were described, as performed in several penetrants including aromatic and aliphatic compounds at 50 and 70 °C. Aromatic penetrants such as toluene and dibutyl phthalate caused sample cracking. For aliphatic penetrants such as heptane, decane, and dodecane, the penetrant transport rate, equilibrium penetrant uptake, and degree of penetrant overshoot were affected by several parameters such as the sample cross-linking ratio, penetrant size, and experimental temperature. The temperature dependence of the polystyrene/dodecane interaction parameter was estimated from the results of dodecane equilibrium uptake for polystyrene samples cross-linked at different levels. Dynamic swelling studies were analyzed with a simple exponential expression. The values of the diffusional exponent indicated that the transport mechanism varied with the sample cross-linking ratio, penetrant chain length, and experimental temperature of each system studied.

Introduction

The study of penetrant transport in glassy polymers has been actively pursued for decades because of its growing significance in polymer processing and related applications. For example, in polymer synthesis, casting and curing operations are limited by the rate at which residual monomers and solvents can be exchanged in or removed from the continuously solidifying polymer phase. In polymer utilization, when a sample is exposed to a solvent, structural failure may occur due to mechanical softening, embrittlement, or crazing. Therefore, application of polymer materials as structural components and as packaging or coating materials requires understanding of how environmental conditions limit material performance.

In the application of glassy polymers in the electronics industry, e.g., data storage media, circuitry encapsulation, and microcircuitry fabrication, it is of importance to investigate how solvents attack and penetrate polymeric materials, under various environmental conditions including high temperatures. In microlithography, it must be studied how a solvent penetrates in a thin, polymeric film where the solvent initiates the rapid dissolution of a polymer resist to create a designed pattern over an electronic substrate. In controlled-release applications, biological fluid penetration can activate the release of bioactive materials loaded in polymer matrices. Control of the biological fluid penetration establishes how well the release rates of such substances can be controlled.

When a penetrant diffuses into a polymer sample, the macromolecular chains rearrange toward new conformations where the rate of relaxation depends on the solvent concentration. The relative rates of penetrant diffusion and macromolecular chain relaxation to new conformations determine the nature of the transport process and lead to a wide variety of penetrant transport phenomena including Fickian, case II,[1] super case II, and anomalous transport.[2-7]

Vrentas, Duda and other collaborators[8-10] defined the diffusional Deborah number, *De*, as a means of characterizing transport processes for penetrant diffusion in polymer systems. This dimensionless group is the ratio of the diffusion time to the relaxation time of polymer chains during the transport process. If the diffusional and the relaxational resistances are of the same order of magnitude, non-Fickian transport is observed.

A generalized expression for the transport kinetics can be written as

$$M_t/M_\infty = kt^n \tag{1}$$

where k is a constant incorporating characteristics of macromolecule and penetrant systems and n is the diffusional exponent, which is indicative of the transport mechanism. The exponent n, associated with values of *De* and the related transport mechanisms, can be affected by the sample geometry.[11]

Numerous experimental studies of penetrant transport in polystyrene[12-24] have been reported. In general, these studies indicate that penetrant transport may be Fickian or non-Fickian (anomalous) and may often lead to unexpected phenomena such as penetrant overshoot or crazing. Overbergh et al.[12] studied dichloromethane and acetone vapor transport in atactic and isotactic polystyrenes and observed that only isotactic polystyrene exhibited overshoot phenomena; they also showed that uptake curves of isotactic and atactic polystyrenes deviated above the critical vapor activity. Isotactic polystyrene showed a decreased sorption rate, gradual desorption, and then loss in transparency ascribed to induced crystallization.

Hopfenberg and co-workers,[13-22] studied the influence of various parameters such as activity, temperature, penetrant structure, sample orientation, filler, sample size, and molecular weight on the transport kinetics and equilibrium uptake of a series of alkane solvents in polystyrene. Normal alkanes from pentane to heptane caused crazing of the samples at high penetrant activities with the kinetics following case II transport. Urdahl and Peppas[23,24] studied the effects of polystyrene cross-linking density and sample size on the sorption kinetics for liquid cyclohexane in cross-linked polystyrene films. Overshoot kinetics were observed in loosely cross-linked samples. Penetrant transport in samples with higher cross-linking ratios indicated a decrease in the amount of overshoot.

In the present contribution, dynamic swelling experiments for a series of cross-linking polystyrenes were performed in several penetrants including both aromatic compounds and alkanes. The effects of polymer cross-linking density, solvent chain length, and temperature on the transport kinetics, sorption rate, overshoot, and cracking or crazing were investigated.

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Table I
Physical Properties of Penetrants Used in Dynamic Swelling Experiments

penetrant	solubility param (cal/cm^3)	density at 25 °C (g/cm^3)	mol wt	bp (°C)
toluene	8.9	0.867	92.14	111
dibutyl phthalate	9.3	1.043	278.30	340
heptane	7.4	0.684	100.21	98
decane	6.6	0.730	142.29	174
dodecane	7.9	0.750	170.34	216.2
cyclohexane	8.2	0.779	84.16	80.8

Experimental Section

1. **Sample Preparation.** A series of cross-linked polystyrene samples was prepared by bulk polymerization. Styrene monomer (St; Aldrich Chemical Co., Milwaukee, MI) was vacuum-distilled at 38 °C (15 mmHg) and was mixed with desired amounts of the cross-linking agent, divinylbenzene (DVB; Aldrich Chemical Co., Milwaukee, WI), at cross-linking ratios, X, of 0.005, 0.01, 0.015, and 0.02 mol of DVB/mol of styrene. The mixtures were reacted in a convection oven at 125 °C for 48 h and then in a vacuum oven at 125 °C for 12 h to remove the unreacted monomer and undesirable impurities. In addition, un-cross-linked polystyrene samples were prepared. Samples were cut in squares using a warm scalpel. All of the samples had an aspect ratio (length over thickness) greater than 10, which ensured application of one-dimensional diffusional equations for analysis of the transport data.

2. **Sample Characterization.** Physical properties of the prepared cross-linked polystyrene were characterized by various techniques. The chemical structure of the sample was determined by transmission FTIR spectrometry (Model 1600; Perkin-Elmer, Norwalk, CT).

Glass transition temperatures were measured by differential scanning calorimetry (Model 910 DSC; Du Pont, Wilmington, DE) with a scanning rate of 10 °C/min at a nitrogen flow rate of 140 mL/min. Thermogravimetric analysis (Model 951 TGA; Du Pont, Wilmington, DE) was performed to observe the thermal stability of a series of cross-linked polystyrene samples. The scanning rate was 25 °C/min, and the nitrogen flow rate was 160 mL/min.

The number-average molecular weight between cross-links, $\bar{M}_c$, was determined by equilibrium swelling experiments in cyclohexane at 45 °C. The equilibrium swelling ratio, Q, and the equilibrium polymer volume fraction in the swollen polymer, v_2 ($=Q^{-1}$), were determined from the values of weights of the unswollen polymer and the swollen polymer samples under the assumption that the volume additivity could be applied.

$$v_2 = \frac{1}{Q} = \frac{W_2/\rho_2 + W_1/\rho_1}{W_2/\rho_2} \qquad (2)$$

Here the subscripts 1 and 2 denote the solvent and polymer. The values of the density of cyclohexane, ρ_1, and of cross-linked polystyrene, ρ_2, were obtained from the experimental data of Cantow and Schuster.[25]

The sol fraction was determined by measuring the weight loss between the initial sample weight and the dry sample weight. The dry sample weight was measured after desorption at room temperature for 1 month, followed by drying at 80 °C for 2 weeks under vacuum.

3. **Dynamic Swelling Experiments.** Dynamic swelling experiments for these samples were performed with several penetrants including aromatic compounds such as toluene and dibutyl phthalate and alkanes such as heptane, decane, and dodecane. Basic properties of the penetrants used in these experiments are presented in Table I. The sample was periodically removed from the constant-temperature bath, blotted dry, and weighed until equilibrium was reached.

Heptane swelling studies were performed at 50 and 70 °C; all other solvent swelling studies were done at 70 °C in order to study the effects of cross-linking density, penetrant size, and other parameters on the transport kinetics, sorption rate, and degree of overshoot. Samples had thicknesses of 0.7–0.9 mm and lengths of 15 mm (see Table II).

Table II
Characteristics of Samples Used for the Dynamic Swelling Experiments

penetrant	exptl temp (°C)	cross-linking ratio, X (mol of DVB/mol of St)	sample wt, M_p (g)	sample thickness, d_0 (mm)
heptane	50	0.005	0.1577	0.73
		0.01	0.1582	0.72
		0.015	0.1594	0.75
		0.02	0.1620	0.78
heptane	70	0.01	0.1618	0.79
		0.015	0.1609	0.73
		0.002	0.1633	0.76
decane	70	0.01	0.1679	0.84
		0.02	0.1655	0.81
dodecane	70	0.01	0.1644	0.81
		0.02	0.1637	0.78

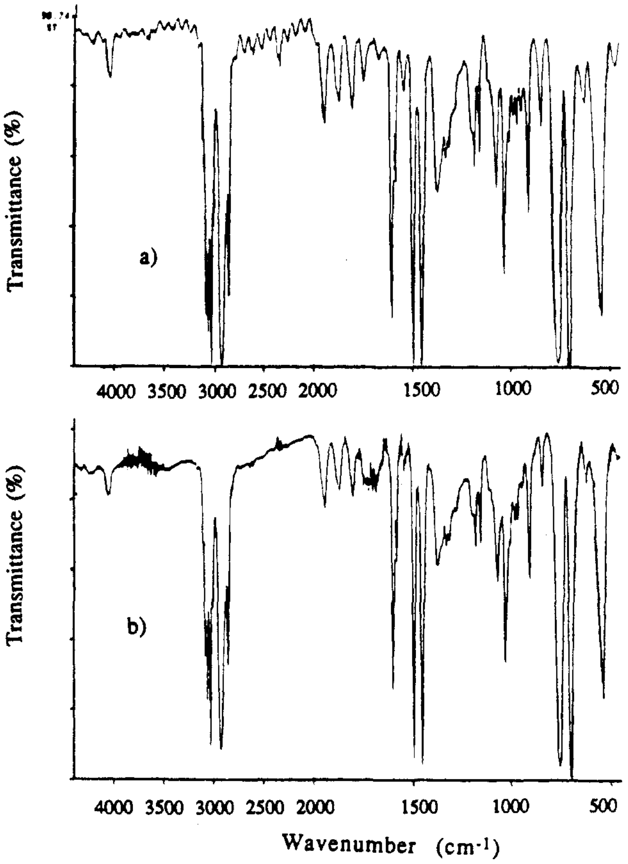

Figure 1. IR spectra of prepared (a) and reference polystyrene (b).

For dodecane swelling studies, experiments were performed at various temperatures, 70, 90, 105, and 120 °C, to investigate the temperature effect on the swelling behavior and to determine the interaction parameter, χ_1, of the cross-linked polystyrene/dodecane system as a function of temperature. The sample thickness was 0.6–0.7 mm for the loosely cross-linked polystyrene ($X = 0.005$ mol/mol) and 1.2–1.3 mm for the densely cross-linked polystyrene samples ($X = 0.01$ mol/mol).

Results

1. **Polystyrene Characterization.** Rectangular polystyrene samples cross-linked at the levels of $X = 0.005$, 0.01, 0.015, and 0.02 mol of DVB/mol of styrene were prepared and characterized.

Figure 1 shows the IR spectra of the prepared linear polystyrene and of the reference polystyrene. The absorption band at 3050 cm^{-1} was the characteristic C–H stretch of the aromatic ring. Two bands around 2900 cm^{-1} were from the C–H stretch and a single band at 1450 cm^{-1}

Table III
Characteristics of Cross-Linked Polystyrene Samples

cross-linking ratio X (mol/mol)	mol wt between cross-links $\bar{M}_c$[a]		sol fraction	glass transition temp T_g (°C)	degradation point T_d (°C)
	$\bar{M}_c$[a]	$\bar{M}_{c,T_g}$[b]			
0.000				93	>250
0.005	5100	5000	<0.01	100.5	>250
0.01	4300	4100	<0.01	101.5	>250

[a] Measured from the swelling experiment. [b] Calculated from T_g.

was from the C–H bend of the aliphatic chains. Other bands were due to the overlapping of several characteristic bonds in polystyrene. The weak bands around 3700 and 1750 cm^{-1} were due to the water absorbed during pelletizing. The IR spectrum of cross-linked polystyrene had absorption bands similar to those of the linear polystyrene.

The glass transition temperature of 95 °C of the prepared linear polystyrene was similar to that of commercial polystyrene.[26] As shown in Table III, the glass transition temperature increased with increasing the cross-linking density. The degradation temperature of the prepared linear polystyrene was 250 °C, being similar to that of reference polystyrene.[26] As shown in Table III, there is no difference between the thermal stability behavior of the linear polystyrene and that of the cross-linked polystyrene.

The cross-linked polystyrene/cyclohexane interaction parameter, χ_1, was obtained from the data of Cantow and Schuster.[25] The value of $\bar{M}_c$ was calculated from an equation developed by Lucht and Peppas.[27,28]

$$\frac{1}{\bar{M}_c} = \frac{2}{\bar{M}_n} - \frac{\bar{\upsilon}[\ln(1-\upsilon_2) + \upsilon_2 + \chi_1\upsilon_2^{\,2}]\left[1 - \frac{\upsilon_2^{\,2/3}}{N}\right]^3}{V_1\left[\upsilon_2^{\,1/3} - \frac{1}{2}\upsilon_2\right]\left[1 + \frac{\upsilon_2^{\,2/3}}{N}\right]^2} \quad (3)$$

$$N = 2\bar{M}_c/M_r$$

Here, $\bar{M}_n$ is the number-average molecular weight of polymer, $\bar{\upsilon}$ is the specific volume of polymer, V_1 is the molar volume of solvent, υ_2 is the equilibrium polymer volume fraction in the swollen gel, and M_r is the molecular weight of the repeating unit. The resulting values of $\bar{M}_c$ decreased with increasing the cross-linking density as shown in Table III. The value of $\bar{M}_c$ determined from the equilibrium swelling experiment was in good agreement with the value of the molecular weight between cross-links calculated from the change in the glass transition temperature between the cross-linked polystyrene and the linear polystyrene, $\bar{M}_{c,T_g}$.[29,30] The sol fraction was less than 0.01 for all samples tested.

2. Toluene and Dibutyl Phthalate Transport. Toluene and dibutyl phthalate are good solvents for polystyrene. Toluene transport created sample cracking 1 h after the beginning of the swelling experiment. The time to induce cracking was different at varying experimental temperatures. As the temperature increased from 30 to 90 °C, the time to induce cracking also increased within 1 h.

Cross-linked polystyrene was easily swollen in dibutyl phthalate; equilibrium uptake was achieved in 12 h. Dibutyl phthalate led to the cracking of the highly cross-linked polystyrene (X = 0.02) after 43 h, but the relatively loosely cross-linked polystyrene (X = 0.005 or 0.01) did not exhibit cracking. Cracking appeared parallel to the edge of the polymer sample.

3. Heptane Transport. Figure 2 shows the results of heptane mass uptake as a function of diffusion time at 50 or 70 °C for polystyrene samples cross-linked at various levels. The heptane transport rate decreased significantly as the cross-linking ratio increased, because the heptane diffusion coefficient is much higher for loosely cross-linked polystyrene. Figure 3 shows the time to achieve the maximum penetrant uptake, t_{max}, as a function of the sample cross-linking ratio at 50 and 70 °C. At 50 °C, t_{max} increased with increasing the cross-linking ratio; its effect was reduced at 70 °C where t_{max} seemed to increase linearly with increasing the cross-linking ratio. It was concluded that the dependence of t_{max} on the sample cross-linking ratio was more significant with decreasing the temperature, especially below the glass transition temperature of the sample.

Figure 4 shows the equilibrium heptane uptake as a function of the sample cross-linking ratio. The highly cross-linked polystyrene sample absorbed less heptane than the loosely cross-linked one. The relation between the equilibrium heptane uptake and the sample cross-

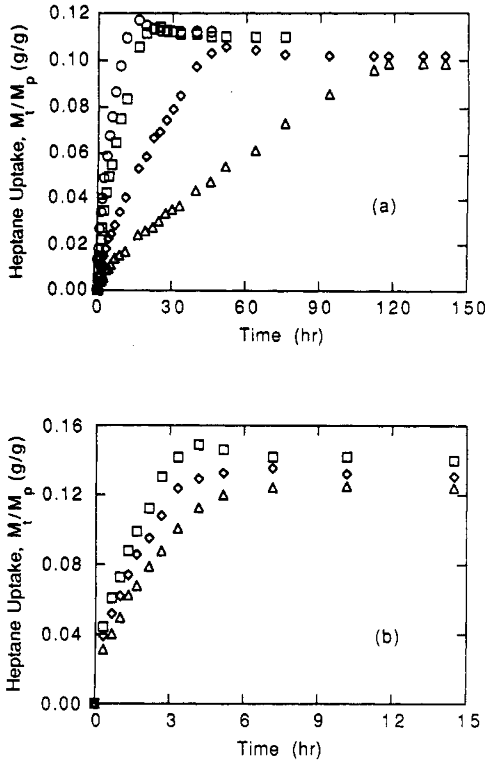

Figure 2. Heptane uptake per polymer weight, M_t/M_p, as a function of diffusion time for cross-linked polystyrene slabs at 50 °C (a) and 70 °C (b). Cross-linking ratios, X, of 0.005 (○), 0.01 (□), 0.015 (◇), and 0.02 (△) mol of DVB/mol of styrene.

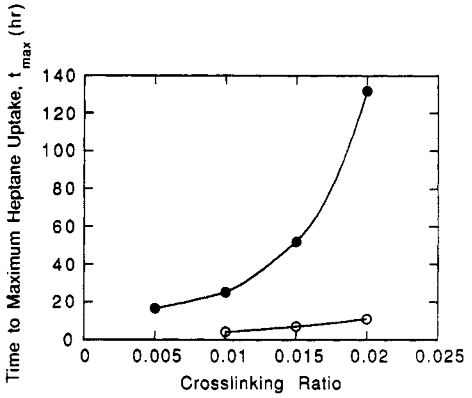

Figure 3. Time to reach the maximum heptane uptake, t_{max}, as a function of the sample cross-linking ratio for polystyrene slabs at 50 (●) and 70 °C (○).

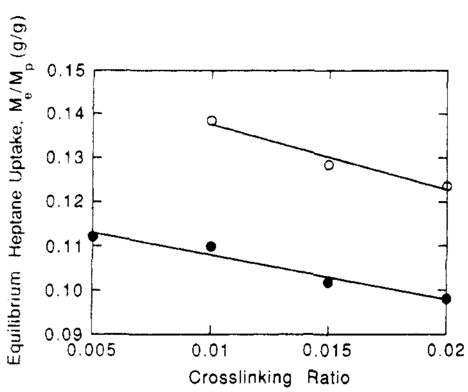

Figure 4. Equilibrium heptane uptake per polymer weight, M_e/M_p, as a function of the sample cross-linking ratio for polystyrene slabs at 50 (●) and 70 °C (○).

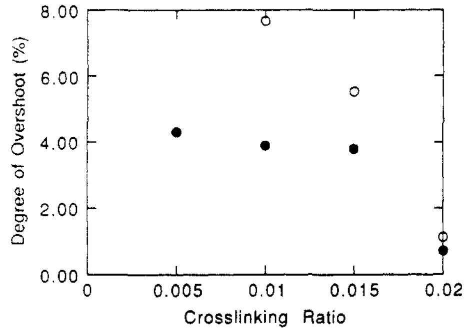

Figure 5. Degree of overshoot as a function of the sample cross-linking ratio for heptane uptake in polystyrene slabs at 50 (●) and 70 °C (○).

linking ratio was linear and temperature independent. Of course, for the same cross-linking ratio, the penetrant uptake was higher at the higher temperature.

Penetrant uptake overshoot was observed with certain samples. The degree of overshoot is defined according to eq 4. Here, M_m and M_e indicate the maximum and

$$\text{degree of overshoot} = \frac{M_m - M_e}{M_e} \times 100 \qquad (4)$$

equilibrium penetrant uptakes, respectively.

As shown from the data of Figure 5, the degree of overshoot decreased with increasing the cross-linking ratio. It is because, in highly cross-linked samples, the relaxational chain rearrangements do not occur as fast as in loosely cross-linked samples. These results are in agreement with the previous studies by Peppas and Urdahl.[23] Similarly, the degree of overshoot was higher at 70 °C than at 50 °C and the cross-linking density effect on the degree of overshoot was more significant at 70 °C.

Figure 6 shows the results of the fractional heptane uptake as a function of the diffusion time in cross-linked polystyrene samples at two temperatures, 50 and 70 °C. A means of characterizing the transport kinetics in these systems involves fitting the data to eq 1. Table IV summarizes the values of the diffusional exponent, n. For transport at 70 °C, the values of n were close to 0.5 for all samples, indicating the Fickian transport process; the values of n did not change much with varying the cross-linking ratio. For transport at 50 °C, the values of the diffusional exponent were between 0.5 and 1, indicating the anomalous transport process; here, the increase in the value of n with increasing the sample cross-linking ratio was apparent.

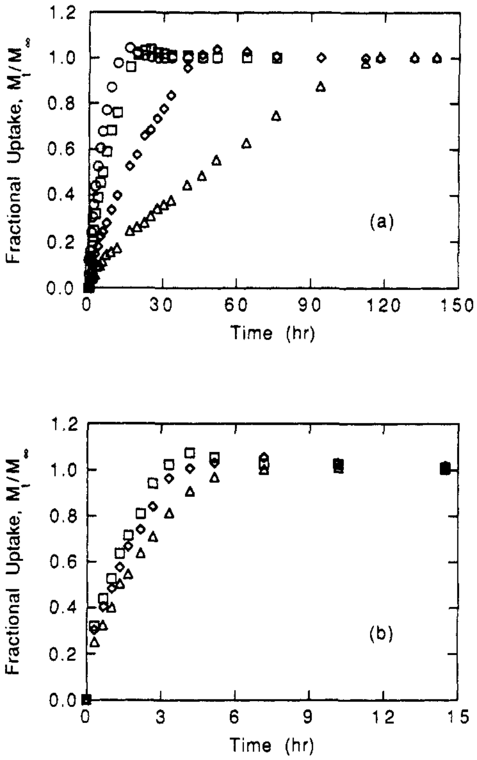

Figure 6. Fractional heptane uptake, M_t/M_∞, as a function of the diffusion time for cross-linked polystyrene slabs at 50 (a) and 70 °C (b). Cross-linking ratios, X, of 0.005 (○), 0.01 (□), and 0.015 (◇), and 0.02 (△) mol of DVB/mol of styrene.

Table IV
Kinetics Analysis of Several Penetrant Transports in Cross-Linked Polystyrene

penetrant	temp (°C)	exponent n	cross-linking ratio (X) (mol of DVB/mol of St)
heptane	50	0.63	0.005
		0.79	0.01
		0.81	0.015
		0.84	0.02
	70	0.50	0.01
		0.50	0.015
		0.52	0.02
decane	70	0.55	0.01
		0.59	0.02
dodecane	70	0.60	0.01
		0.66	0.02

4. Transport of a Series of Alkanes. The dynamic swelling experiments of cross-linked polystyrene in a series of alkanes such as heptane, decane, and dodecane were performed at 70 °C. Figure 7 presents the results of penetrant uptake as a function of time for these penetrants in the polystyrene samples cross-linked at different levels. Increasing the penetrant size resulted in decreasing the transport rate which was more prominent for the highly cross-linked polystyrene samples. The time to reach the maximum penetrant uptake increased exponentially with increasing penetrant chain length as shown in Figure 8. There was a linear relation between the log t_{max} and penetrant chain length, but the dependence of this relationship on the sample cross-linking ratio was negligible.

Equilibrium penetrant uptake decreased linearly with increasing the penetrant chain length as shown in Figure 9, and the cross-linking level of the sample did not affect much on this relation. For a fixed penetrant, the value of M_e/M_p for the lightly cross-linked sample was higher than that for the highly cross-linked ones.

The effect of the penetrant chain length on the degree of overshoot was observed in Figure 10 for the two different cross-linked polystyrene samples. The degree of overshoot

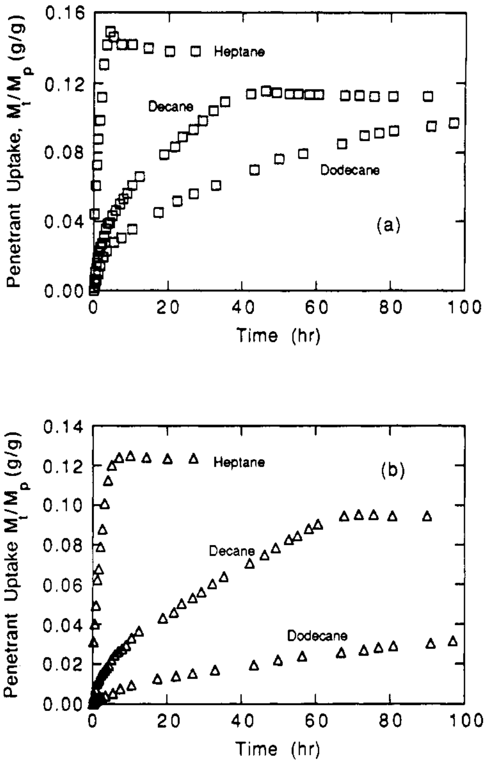

Figure 7. Penetrant uptake per polymer weight, M_t/M_p, as a function of diffusion time at 70 °C for heptane, decane, and dodecane transport in polystyrene samples cross-linked at 0.01 (a) and 0.02 (b) mol of DVB/mol of styrene.

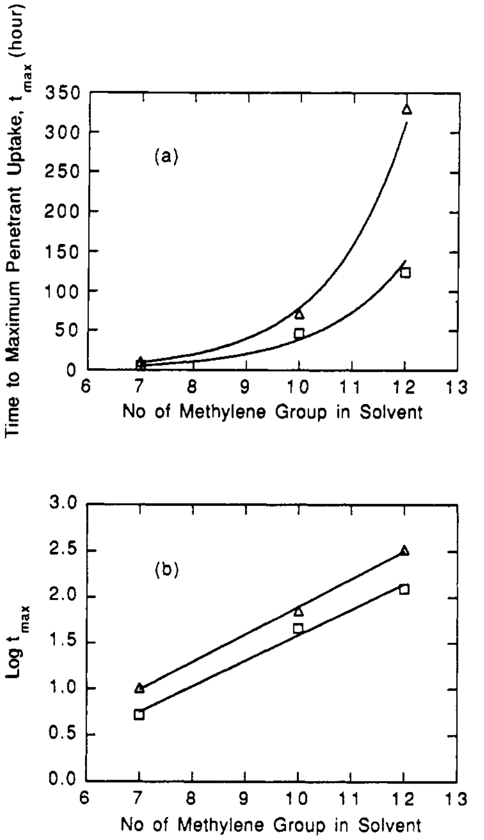

Figure 8. Time to reach the maximum penetrant uptake, t_{max}, as a function of the penetrant chain length for polystyrene slabs at 70 °C. Cross-linking ratios, X, of 0.01 (□) and 0.02 (△) mol of DVB/mol of styrene.

seemed to decrease with increasing the penetrant chain length. The variation of penetrant size did not influence much the degree of overshoot for highly cross-linked samples.

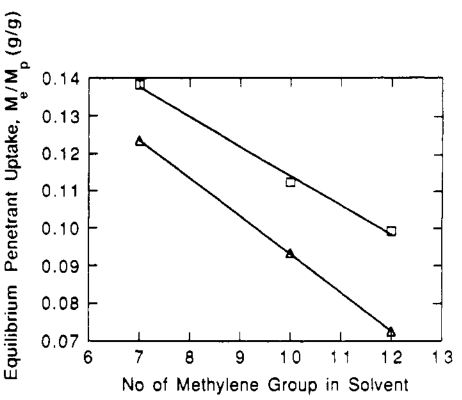

Figure 9. Equilibrium penetrant uptake per polymer weight, M_e/M_p, as a function of the penetrant chain length for polystyrene slabs at 70 °C. Cross-linking ratios, X, of 0.01 (□) and 0.02 (△) mol of DVB/mol of styrene.

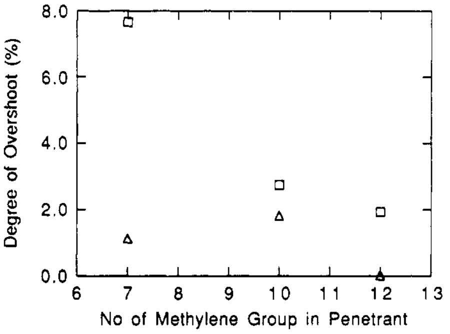

Figure 10. Degree of overshoot as a function of the solvent chain length for heptane uptake in polystyrene slabs 70 °C. Cross-linking ratios, X, of 0.01 (□) and 0.02 (△) mol of DVB/mol of styrene.

From the data of fractional uptake of heptane, decane, and dodecane as a function of time for polystyrene samples cross-linked at different levels, the values of exponent n were calculated and shown in Table IV. At 70 °C, the values of n for polystyrene cross-linked at constant level increased slightly as the penetrant chain length increased.

5. Dodecane Transport at Various Temperatures. Dodecane transport behavior in polystyrene samples cross-linked with 0.005 and 0.01 mol of DVB/mol of styrene was observed at four different temperatures of 70, 90, 105, and 120 °C. The un-cross-linked polystyrene was slowly dissolved in dodecane at all temperatures.

Figure 11 shows the results of dodecane uptake, M_t/M_p, as a function of time. In general, the transport rate increased with increasing the swelling temperature. The transport rate rapidly increasing with increasing the temperature, and the transport rates at the temperatures of 105 and 120 °C that were above the glass transition temperature of dodecane free polystyrene did not show significant difference.

It was observed as shown in Figure 12 that the time to reach maximum mass uptake, t_{max}, decreased exponentially with increasing the temperature in both the glassy and rubbery regions of the polymer. The cross-linking density did not influence greatly this relationship.

The equilibrium penetrant uptake linearly increased with increasing the temperature as shown in Figure 13. From the results of the equilibrium swelling experiments in dodecane, we could determine the polystyrene/dodecane interaction parameter, χ_1, as a function of temperature for the two cross-linked polystyrenes used (X = 0.005 and 0.01). As the value of M_c had already been determined from the equilibrium swelling experiments in cyclohexane, the χ_1 value for the present system could be determined

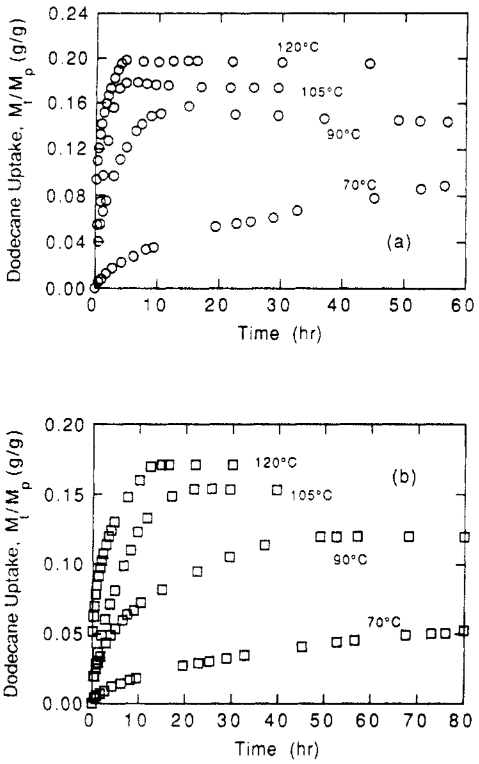

Figure 11. Dodecane uptake per polymer weight, M_t/M_p, as a function of diffusion time at different experimental temperatures, 70, 90, 105, and 120 °C, for polystyrene slabs cross-linked at 0.005 (a) and 0.01 (b) mol of DVB/mol of styrene.

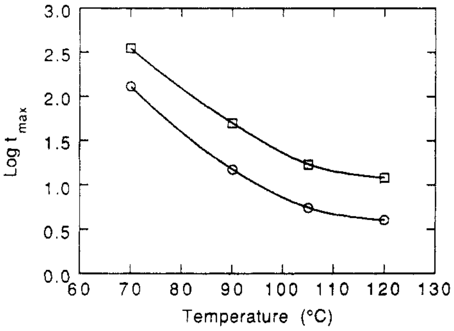

Figure 12. Time to reach the maximum dodecane uptake, t_{max}, as a function of the experimental temperature for polystyrene slabs. Cross-linking ratios, X, of 0.005 (○) and 0.01 (□) mol of DVB/mol of styrene.

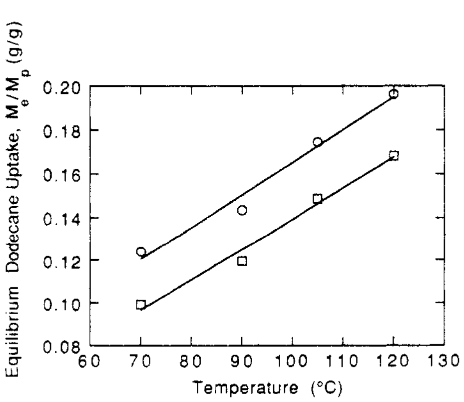

Figure 13. Equilibrium dodecane uptake per polymer weight, M_e/M_p, as a function of the experimental temperature for polystyrene slabs. Cross-linking ratios, X, of 0.005 (○) and 0.01 (□) mol of DVB/mol of styrene.

by rearrangement of eq 1. The value of the equilibrium polymer volume fraction, ν_2, for the present system was obtained from eq 2 by using the equilibrium dodecane uptake, M_e, and the polymer sample weight, M_p, instead of W_1 and W_2. The densities of the cross-linked polystyrene and of dodecane at each temperature were obtained from other experimental data.[31]

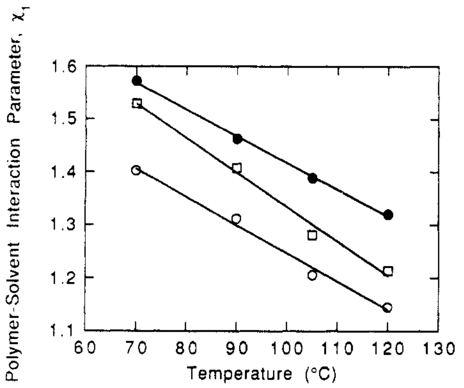

Figure 14. Polystyrene/dodecane interaction parameter as a function of temperature. Cross-linking ratios, X, of 0.005 (○) and 0.01 (□) mol of DVB/mol of styrene.

Figure 14 shows the variation of the polystyrene/dodecane interaction parameter as a function of temperature. The reference data (●) indicate the extrapolated value of the interaction parameter to the present experimental conditions for the un-cross-linked polystyrene/dodecane system determined by DiPaola-Baranyi and Guillet.[32] In general, the χ_1 value decreases with increasing the temperature. The difference between the values of χ_1 in the present system and reference system is 10–15% of the original value. At constant temperature, the χ_1 value for the highly cross-linked polystyrene is higher than that for the loosely cross-linked one.

Discussion

Toluene uptake generated sample cracking regardless of the cross-linking level at all experimental temperatures. For dibutyl phthalate uptake, cracking was observed only for highly cross-linked samples. This cracking was caused by the difference between the relaxation and diffusion rates at the experimental conditions. Because the relaxation rate was not as fast as the diffusion rate for such highly cross-linked polymers swollen in good solvents such as toluene and dibutyl phthalate, the stress generated cracking. These phenomena became more significant as the temperature decreased or the cross-linking ratio increased.

The transport rate increased with decreasing the cross-linking level of the polymer sample or penetrant size and increasing the temperature. The decrease in the sample cross-linking ratio led to an increase in the polymer chain mobility and free volume, resulting in the fast penetrant transport and high equilibrium uptake in the polymer sample. The change of the alkane size led to the increasing resistance in the diffusion of the longer chain of solvent penetrating through the polymer sample which had a constant free volume. The temperature effect on the transport rate and equilibrium penetrant uptake was similar to the effect of the cross-linking density and penetrant chain length. At the higher experimental temperature, the increase in the diffusion and relaxation rates of the polymer, accompanied by the increase in the polymer free volume resulted in a higher equilibrium penetrant uptake.

The degree of overshoot decreased slightly with increasing the penetrant size or increasing the sample cross-linking ratio at constant temperature. Highly cross-linked samples have such a low flexibility of the chain segment that the rate of relaxation is not high. Therefore, the conformational chain rearrangement of polymer molecules for the loosely cross-linked polystyrene involving the alkane which has a shorter chain length is much faster than that for the opposite system. This degree of chain rearrangement after the maximum penetrant uptake controls the degree of overshoot caused by the penetrant rejection during relaxation. In addition, overshoots are known to be related to geometrical factors such as thickness of the sample.[23]

The transport kinetics was also affected by several parameters. From the results of Hopfenberg and associates[13,14,33] on the heptane uptake in polystyrene film and sheet, it was observed that the transport kinetics changed from Fickian to case II, as the activity increased and the temperature decreased. In the present experimental conditions, the value of the diffusional exponent, n, generally increased with increasing the sample cross-linking ratio or penetrant chain length or decreasing the experimental temperature, especially when the temperature was below the glass transition temperature. Therefore, it is difficult to characterize the overall transport kinetics with a specific experimental parameter. It is shown that the changes in the transport kinetics are caused by the change in the relative rate between the polymer chain relaxation and the penetrant diffusion during the penetrant uptake. In the present experimental conditions, the transport kinetics for the system of alkane transport in cross-linked polystyrene was characterized from Fickian to case II by increasing the cross-linking ratio, increasing the penetrant size and mainly decreasing the temperature below the glass transition temperature.

Acknowledgment. This work was supported in part by a grant from the National Science Foundation.

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